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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>5</sup> :  C08F 20/12, 2/22	A1	(11) International Publication Number: WO 92/00335 (43) International Publication Date: 9 January 1992 (09.01.92)
<p>(21) International Application Number: PCT/GB91/00964</p> <p>(22) International Filing Date: 14 June 1991 (14.06.91)</p> <p>(30) Priority data: 90307147.0 29 June 1990 (29.06.90) GB</p> <p>(71) Applicant (for CA only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).</p> <p>(71) Applicant (for all designated States except CA US): VINAMUL LIMITED [GB/GB]; Mill Lane, Carshalton, Surrey SM5 2JU (GB).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): FARMER, David, Bretland [GB/GB]; Spring Cottage, Sutton Place, Abinger Hammer, Dorking, Surrey RH5 6RP (GB). McLENAN, Alistair, John [GB/GB]; 139 Shaftesbury Road, Carshalton, Surrey SM5 1HJ (GB).</p>		<p>(74) Agent: KEITH W. NASH &amp; CO.; Pearl Assurance House, 90-92 Regent Street, Cambridge CB2 1DP (GB).</p> <p>(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), LU (European patent), NL (European patent), SE (European patent), US.</p> <p><b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: EMULSION POLYMERISATION</p> <p>(57) Abstract</p> <p>A copolymer emulsion suitable for use as a sizing agent for glass fibre is formed by microfluidising an emulsion containing at least 90 % by weight of C1 to C10 alkyl(meth)acrylate monomer and stabilised by a protective colloid, e.g. polyvinyl alcohol, prior to initiation of the polymerisation reaction.</p>		

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Title: Emulsion Polymerisation

Field of the invention

This invention relates to copolymer emulsions, and particularly concerns copolymer emulsions suitable for use as sizing agents for glass fibre prior to incorporation of bulk glass fibre in thermoplastic polymers.

Background to the invention

Glass fibre is a form of glass produced by a technique in which molten glass is passed through a multi apertured mould to form filaments. These filaments have small diameters usually in the range of 1 micron to 4 micron, typically about 2 micron, although diameters outside this range are known for special applications. These filaments are then subjected to a sizing operation, using a sizing agent, possibly in combination with other additives, to provide bonding of the filaments together to form strands or fibres.

One application of glass fibres is to provide reinforcement and flexibility to thermoplastic polymer articles, typically made of polymers such as polypropylene, polyamides and polycarbonates, and usually shaped by injection moulding.

The sizing agent additionally functions to protect the filaments from breaking during handling, and must also be

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capable of withstanding the heat applied, e.g. up to 200°C, during contact with the polymeric material to be reinforced.

#### Summary of the invention

In one aspect the present invention provides a copolymer emulsion containing from 20% to 70%, preferably 45 to 60%, by weight solids which comprise copolymer particles having a weight mean particle diameter from about 0.05 micron to about 1.5 micron, stabilised by a protective colloid, e.g. polyvinylalcohol, comprising at least about 90% by weight of C1 to C10 alkyl(meth)acrylate monomer to provide a polymer-glass transition temperature (T<sub>g</sub>) in the range from about 0°C to about 60°C, preferably from about 20°C to about 50°C. The use of the particle sizes quoted allows the preparation of a stable emulsion which is of particular use as a sizing agent suitable for glass fibre; use of larger particles may have a detrimental effect on strand integrity.

The invention thus enables production of acrylate copolymer emulsions suitable for use as a glass fibre sizing agent, which has not hitherto been possible. Acrylates have better properties of heat resistance than materials conventionally used as sizing agents, e.g. vinyl acetate emulsion polymers, and so are better suited to this application.

The T<sub>g</sub> quoted is the effective T<sub>g</sub> and this could be provided either by suitable choice of monomers, or by addition of a plasticiser, e.g. dibutyl phthalate, to a mixture that would otherwise produce a polymer having a T<sub>g</sub> above the specified range.

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To obtain the most efficient sizing of glass filaments, the emulsion should be free of particles above 2 microns, and preferably has a weight mean particle diameter of above about 0.2 micron, more preferably above about 0.4 micron. Mean weight particle diameters of the copolymer particles are typically in the range of 0.4 to 1.0 micron.

Examples of the acrylate monomers are methyl methacrylate (homopolymer Tg of 100°C), ethylhexyl acrylate (Tg of -60°C), butyl acrylate (Tg of -50°C) and ethyl acrylate (Tg of -22°C). A proportion of a carboxylic monomer, for example acrylic acid, may also be present to improve adhesion to the surface of glass. Other monomers may be incorporated at minor levels, that is up to 10% by weight of the total monomers, usually up to 5%. Examples of these monomers are vinyl silanes, cross linking agents and epoxy monomers, e.g. glycidylmethacrylate. The cross linking agents may be capable of internal cross linking, e.g. diallyl maleate, triallyl cyanurate or crosslinkable, e.g. N-methylolacrylamide.

The acrylate monomer is generally initially present in the form of an emulsion which requires to be stabilised by a protective colloid, and the preferred colloid material is polyvinyl alcohol. There is no criticality in the degree of hydrolysis of polyvinyl alcohol; preferably the degree of hydrolysis is above 70%, and the degree of polymerisation is preferably above 550.

Other protective colloids which can be used include hydroxyethyl cellulose, carboxymethyl cellulose, ethoxylated starch derivatives, polyacrylates, acrylamides, gelatins, alginates, gums and agar.

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The protective colloid will usually be present in an amount from about 1% to about 5% by weight of monomer present.

A surfactant may be present to assist in stabilising monomer droplets, and preferably an oil compatible solvent, for example a long chain alkane, e.g. hexadecane, is present in the droplets to stabilise the monomers.

Polymerisation can be achieved using any suitable initiation system: the system used is not critical, but it is preferred that the system is oil soluble.

The desired particle size can be achieved by subjecting an emulsion including monomers and protective colloid, e.g. polyvinyl alcohol, to a microfluidisation step, for example with the aid of sonication or an impinging jet device, prior to initiation. In a sonication device, high intensity sound waves are introduced into the emulsified monomer feedstock. In an impinging jet device a pump, for example an electric pump or an air driven piston, produces a high static liquid pressure, e.g. up to 1400 bar, with the aid of air at pressure of 6 bar. The pump forces the emulsified monomers through a ceramic interaction chamber at high velocity. In this chamber the flow is divided into two streams which are forced through narrow slits to impinge together. At the point of impingement a volume of intense turbulence is created causing a release of energy as cavitation and shear forces. Jet impingement devices of this type can be obtained from Microfluidics Corporation of Newton Mass. USA.

The conventional features in the preparation the copolymer emulsions of the invention are well characterised in the literature. Polymer Synthesis (vols I and II) by Sandler &

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Karo (Academic Press 1974) and Preparative Methods of Polymer Chemistry (2nd Ed) by Sorenson & Campbell (Interscience 1968) provide preparative information. Methoden der Organischen Chemie (Houben-Weyl) Band XIV published by Georg Thieme Verlag Stuttgart (1961) also provides preparative descriptions. However these general disclosures do not provide information on the formation of the small particle size emulsions to which the present invention is directed.

The invention also provides a method of preparing a copolymer emulsion in accordance with the invention, wherein monomer feedstock is prepared in emulsion form stabilised by a protective colloid, characterised in that prior to initiation the emulsion is subjected to a microfluidisation step to reduce the emulsion average particle size to be in the range 0.05 micron to 1.5 micron.

The invention also includes within its scope the use of a copolymer emulsion in accordance with the invention as a size for glass fibre, wherein an effective amount of the emulsion is applied to the glass fibre prior to the latter being incorporated into a thermoplastic article.

Also within the scope of the invention are glass fibre and thermoplastic materials and articles produced in this way.

#### Test Methods

Particle size distribution: the weight mean particle diameter  $D(v0.5)$  was measured using a Malvern Mastersizer, which employs a laser light scattering technique using very dilute emulsion samples.

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Viscosity: a Brookfield viscometer type RVT was used with a spindle No.1 and speed (rpm) of 20. Measurements were made at 25°C.

Weight loss: films were cast and dried for 3 days at ambient temperature. They were then weighed and heated to 200°C for 10 minutes and 30 minutes with the weight loss being measured after each period.

### Specific Description of the Invention

Examples of the process of the invention will now be given to illustrate but not limit the invention.

### Examples 1 - 6

Oil phase A and aqueous phase B having the compositions given below were prepared separately and then mixed with each other and pre-emulsified using a Greaves mixer (model B) obtained from Joshua Greaves & Sons of Ramsbottom England on full power (9,500 rpm) for 1 minute.

### Phase A

methy methacrylate	190g
ethyl hexyl acrylate	60g
Interox BCHPC 75W*	0.5g
dilauroyl peroxide	0.17g
hexadecane	3.0g

\* This is bis (4-t-butylcyclohexyl)peroxydicarbonate.

These initiators (Interox and dilauroyl peroxide) are oil soluble.



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Phase B

polyvinyl alcohol GL05 **	4.5g
polyvinyl alcohol KL05 **	4.5g
water	252.45g
surfactant	
(A,B,C,D or E - see below)***	
antifoam	2 drops

\*\* The polyvinyl alcohols were obtained from Nippon Gohsei KK of Japan. GL05 is 88% hydrolysed and KL05 80% hydrolysed. Each has a degree of polymerisation of 600.

\*\*\* Surfactant was present in an amount 0.5% active on monomer weight.

The pre-emulsion obtained by mixing phases A and B was then processed through a jet impingement microfluidiser (type M110T obtained from Microfluidics Corp.) using one pass at 5 bar air pressure. The gauge registered a hydraulic pressure 893 to 939 bar as the pump operated. This resulted in production of a microfluidised emulsion.

For examples 1-3, 20% of the microfluidised emulsion was polymerised at 70°C for 1 hour, then the remaining microfluidised emulsion was added continuously over 3 hours, maintaining the polymerisation temperature at 70°C and holding the temperature for 15 minutes after additions were complete.

For examples 4-6, 40% of the microfluidised emulsion was polymerised at 70°C for 0.5 hours, then the remaining microfluidised emulsion was added continuously over 1.5 hours, maintaining the polymerisation temperature at 70°C

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and holding the temperature for a further 30 minutes after additions were complete.

Different surfactants A-E were used in the different examples.

After the holding period in each experiment, the temperature was reduced to 50°C and a solution of sodium metabisulphite (0.25g in 5g water) was added, followed by a solution of t-butylhydroperoxide (0.25g in 5g water). All batches were made at 50% theoretical non-volatiles (nv) and had a theoretical Tg of 40°C.

Table I

Example	Surfactant	nv(%)	pH	Viscosity	Monomer Size (u)
1	A	49.02	4.02	4.94	0.38
2	B	49.00	3.98	1.03 #	0.43
3	C	49.05	5.86	2.48	0.49
4	C	48.90	6.01	3.52	0.43
5	D	48.90	4.90	3.05	0.74
6	E	49.29	4.31	1.26	0.46

#measured at 50 rpm.

Surfactants A to E were:

A Empicol LXV: Sodiumlauryl sulphate obtained from Albright & Wilson of England.

B Synperonic NP30: Nonylphenylethoxylate, 30 EO obtained from ICI Ltd of England

C Aerosol A22n: Tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl-sulphonsuccinamate

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obtained from Cyanamid Corp USA

D Aerosol A268: Disodium isodecylsulphosuccinate

E Soprofor 40: Tristyrylphenylethoxylate 20 EO obtained from Rhone Poulenc of France

Weight mean particle diameters (in micron) of the monomer droplets are shown in Table I, and weight mean particle diameters (in micron) of the polymer emulsion latices are shown in Table II together with weight losses after heating at 200°C.

Table II

Expt	latex Particle size (u)	Weight loss at 200°C	
		10 min	30 min
		(%)	(%)
1	0.43	2.37	2.97
2	0.57	1.41	2.08
3	0.54	1.29	1.95
4	0.46	1.35	2.18
5	0.46	1.63	2.55
6	0.53	1.40	2.24

The particle size of the latices are seen to be in the range which makes them suitable as glass fibre sizes. The small weight losses at 200°C demonstrate the thermal stability of the products and hence suitability for use as sizing agents for glass fibre for incorporation in thermoplastic polymer articles.

Example 7

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The procedure of examples 1 to 3 was repeated generally as described above, with the following modification. After the holding period the temperature was reduced to 50°C and a solution of sodium metabisulphite (0.75g in 15g water) was added, followed by a solution of t-butylhydroperoxide (0.75g in 15g water).

In this example, phases A and B had the following compositions:

Phase A

methyl methacrylate	506g
ethyl hexyl acrylate	244g
Interox BCHPC 75W	1.5g
dilauroyl peroxide	0.51g
hexadecane	9.0g

Phase B

polyvinyl alcohol GL05	13.5g
polyvinyl alcohol KL05	13.5g
water	757.4g
surfactant C(45% aq.soln.)	8.4g
antifoam	6 drops

The resulting product had a theoretical Tg of 22°C and the following other properties:

nv(%)	pH	Viscosity	Particle Size	Particle Size
			monomer (micron)	latex (micron)
50.10	6.32	1.73	0.59	0.46

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The emulsions obtained from these experiments are thus suitable for use as sizing agents for glass fibres. In a typical method for producing glass fibre, glass filaments are drawn down from casting tank orifices and the filaments are contacted with the emulsion size via an application roller wheel or other contact means, resulting in bonding of the filaments together to form strands of fibres. The fibres are then wound on a collet to form a cake of glass fibres which is then dried. The emulsion size will usually have a solids content of 2% to 5% and may contain additives such as lubricants and coupling agents which are well known to the skilled user.

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Claims

1. A copolymer emulsion containing from 20% to 70% by weight solids which comprise copolymer particles having a weight mean particle diameter in the range about 0.05 micron to about 1.50 micron, stabilised by a protective colloid, comprising at least about 90% by weight of C1 to C10 alkyl(meth)acrylate monomers to provide a Tg in the range from about 0°C to about 60°C.
2. A copolymer emulsion according to claim 1, wherein the copolymer particles have weight mean particle diameter above about 0.2 micron.
3. A copolymer emulsion according to claim 2, wherein the copolymer particles have a weight mean particle diameter in the range 0.4 micron to 1.0 micron.
4. A copolymer emulsion according to claim 1, 2 or 3, wherein the protective colloid is polyvinyl alcohol.
5. A method of preparing a copolymer emulsion according to claim 1, wherein monomer feedstock is prepared in emulsion form stabilised by a protective colloid, characterised in that prior to initiation the emulsion is subjected to a microfluidisation step to reduce the emulsion average particle size to be in the range 0.05 micron to 1.5 micron.
6. A method according to claim 5, wherein the average particle size of the emulsion is above about 0.2 micron.

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7. A method according to claim 6, wherein the average particle size of the emulsion is in the range 0.4 microns to 1.0 micron.

8. A method according to claim 5, 6 or 7, wherein the protective colloid is polyvinyl alcohol.

9. A method according to any one of claims 5 to 8, wherein the microfluidisation is achieved by an impinging jet device.

10. The use of the copolymer emulsion of any one of claims 1 to 4 as a size for glass fibre wherein an effective amount of the emulsion is applied to the glass fibre prior to the latter being incorporated into a thermoplastic article.

# INTERNATIONAL SEARCH REPORT

International Appli      a No      PCT/GB 91/00964

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC Int.C1.5                      C 08 F 20/12                      C 08 F 2/22											
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border: 1px solid black; padding: 2px;">Minimum Documentation Searched<sup>7</sup></div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; padding: 5px;">Classification System</th> <th style="padding: 5px;">Classification Symbols</th> </tr> <tr> <td style="padding: 5px;">Int.C1.5</td> <td style="padding: 5px;">C 08 F</td> </tr> </table> <div style="text-align: center; padding: 5px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched<sup>8</sup></div>			Classification System	Classification Symbols	Int.C1.5	C 08 F					
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Int.C1.5	C 08 F										
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; padding: 5px;">Category<sup>9</sup></th> <th style="width: 70%; padding: 5px;">Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 20%; padding: 5px;">Relevant to Claim No.<sup>13</sup></th> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">EP,A,0273605 (LION CORP.) 6-July 1988, see claim 1; page 19, line 30 - page 20, line 11; example 1 -----</td> <td style="text-align: center; vertical-align: top; padding: 5px;">-1-10</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">NL,A,6510472 (DUPONT) 14 February 1966, see claim 1 -----</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-9</td> </tr> </table>			Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	X	EP,A,0273605 (LION CORP.) 6-July 1988, see claim 1; page 19, line 30 - page 20, line 11; example 1 -----	-1-10	X	NL,A,6510472 (DUPONT) 14 February 1966, see claim 1 -----	1-9
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>9</sup> Special categories of cited documents : <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>											
<b>IV. CERTIFICATION</b> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;">           Date of the Actual Completion of the International Search   <div style="text-align: center;">24-09-1991</div> </td> <td style="width: 50%; padding: 5px;">           Date of Mailing of this International Search Report   <div style="text-align: center;">06.11.91</div> </td> </tr> <tr> <td style="width: 50%; padding: 5px;">           International Searching Authority   <div style="text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="width: 50%; padding: 5px;">           Signature of Authorized Officer   <div style="display: flex; justify-content: space-between;"> <span>Falk Heck</span> </div> </td> </tr> </table>			Date of the Actual Completion of the International Search  <div style="text-align: center;">24-09-1991</div>	Date of Mailing of this International Search Report  <div style="text-align: center;">06.11.91</div>	International Searching Authority  <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer  <div style="display: flex; justify-content: space-between;"> <span>Falk Heck</span> </div>					
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9100964

SA 48446

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 07/10/91  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0273605	06-07-88	JP-A- 63270850	08-11-88
		JP-A- 63270871	08-11-88
		JP-A- 63266408	02-11-88
		JP-A- 63270369	08-11-88
		JP-A- 63268774	07-11-88
		JP-A- 63270891	08-11-88
		JP-A- 63270892	08-11-88
		JP-A- 63264678	01-11-88
		JP-A- 63311358	20-12-88
		JP-A- 63311347	20-12-88
		US-A- 4943612	24-07-90
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